# Natural Gas Sweetening Process Design

## Kurt Mearkeltor

MSc in Chemical Engineering and candidate to PhD in Chemical Engineering at the
Department of Science of the School of Doctoral Studies of the EU

Email: k.mearkeltor@dsc.sds.eu

## Abstract

For decades to come, gas will be the energy source of choice to meet worldwide environmental standards. Fortunately gas reserves are growing; but new gas is often found to be of substandard quality in remote and / or stranded areas of the world. When natural wellhead or oil field associated gases are highly loaded with acid gases, the dilemma facing most operators is what to do, how and when to best exploit these poor quality resources. Today the advanced activated MDEA process offers economy and versatility in handling both selective and complete acid gas removal services. The process has a good synergy with modern Claus sulfur recovery processes and remains among the best alternatives even when no sulfur recovery is foreseen. Nevertheless, there are limitations of even the most advanced amines only based gas treatment technologies in handling very highly acid gas loaded natural or associated oil field gases; especially for bulk acid gas removal when the acid gases are destined for cycling and / or disposal by reinjection. Today cycling and disposal by re-injection offers a promising alternative to avoid sulfur production and reduce CO2 emissions to the atmosphere simultaneously. To this end, technologies of choice are those which offer maximum simplicity and require least downstream processing intensity and power for re-injection. **Keywords:** Chemical Engineering; Natural Gas Sweetening Process.

Natural gas from high-pressure wells is usually passed through field separators at the well to remove hydrocarbon condensate and water (Kirk & Othmer 1951). Natural gasoline, butane, and propane are usually present in the gas, and gas-processing plants are required for the recovery of these liquefiable constituents (Kirk & Othmer 1951).

Natural gas is considered "sour" if hydrogen sulfide ($H_2S$) is present in amounts greater than 5.7 milligrams per normal cubic meters (mg/Nm) (0.25 grains per 100 standard cubic feet [gr/100 scf]) (Maddox 1974). The $H_2S$ must be removed (called "sweetening" the gas) before the gas can be utilized. If $H_2S$ is present, the gas is usually sweetened by absorption of the $H_2S$ in an amine solution (Maddox 1974). Amine processes are used for over 95 percent of all gas sweetening in the United States. Other methods, such as carbonate processes, solid bed absorbents, and physical absorption, are employed in the other sweetening plants. Emission data for sweetening processes other than amine types are very meager, but a material balance on sulfur will give accurate estimates for sulfur dioxide ($SO_2$) (Mullins 1975).

The major emission sources in the natural gas processing industry are compressor engines, acid gas wastes, fugitive emissions from leaking process equipment, and if present, glycol dehydrator vent streams. Fugitive leak emissions are detailed in *Protocol For Equipment Leak Emission Estimates* (EPA 1995). Regeneration of the glycol solutions used for dehydrating natural gas can release significant quantities of benzene, toluene, ethyl benzene, and xylene, as well as a wide range of less toxic organics. These emissions can be estimated by a thermodynamic software model (*GRI-GLYCalc*), available from the Gas Research Institute.

Many chemical processes are available for sweetening natural gas. At present, the amine process (also known as the Girdler process) is the most widely used method for $H_2S$ removal. The process is illustrated below:

$$2\ RNH_2\ H_2S\ (RNH_3)_2\ S$$

Where:
- R = mono, di, or tri-ethanol
- N = nitrogen
- H = hydrogen
- S = sulfur

(Katz et al. 1959).

The recovered hydrogen sulfide gas stream may be: (1) vented, (2) flared in waste gas flares or modern smokeless flares, (3) incinerated, or (4) utilized for the production of elemental sulfur or sulfuric acid (EPA 1970).

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Fortunately gas reserves are growing; but new gas is often found to be of substandard quality in remote and / or stranded areas of the world. When natural wellhead or oil field associated gases are highly loaded with acid gases, the dilemma facing most operators is what to do, how and when to best exploit these poor quality resources.

Today the advanced activated MDEA process offers economy and versatility in handling both selective and complete acid gas removal services. The process has a good synergy with modern Claus sulfur recovery processes and remains among the best alternatives even when no sulfur recovery is foreseen (Blanc et al. 1981).

Nevertheless, there are limitations of even the most advanced amines only based gas treatment technologies in handling very highly acid gas loaded natural or associated oil field gases; especially for bulk acid gas removal when the acid gases are destined for cycling and / or disposal by reinjection (Elgue, Peytavy, & Tournier-Lasserve 1991). Today cycling and disposal by re-injection offers a promising alternative to avoid sulfur production and reduce $CO_2$ emissions to the atmosphere simultaneously. To this end, technologies of choice are those which offer maximum simplicity and require least downstream processing intensity and power for re-injection (Elgue, Peytavy, & Tournier-Lasserve 1991).

The behavior of $CO_2$ and $H_2S$ in combination with water at high pressures and at temperatures within process operating conditions can result in hydrate formation, liquid phases of the compounds, and large variations in the amount of absorbed water. Since similar experimental data for mixtures of acid gases and water are not always readily available in the public literature, it is necessary to rely on computer generated results for mixtures for designing compression and injection facilities, which may not be entirely accurate (Royan & Wichert 1995).

Natural gas reservoirs have always been associated with water; thus, gas in the reservoir is water saturated. When the gas is produced water is produced as well. Some of this water is produced water from the reservoir directly (Sharma & Campbell 1969). Other water produced with the gas is water of condensation formed because of changes in temperature and pressure during production.

In the sweetening of natural gas, the removal of hydrogen sulfide and carbon dioxide, aqueous solvents are usually used (Sharma & Campbell 1969). The sweetened gas, with the $H_2S$ and $CO_2$ removed, is saturated with water. In addition, the acid gas byproduct of the sweetening is also saturated with water. Furthermore, water is an interesting problem in the emerging technology for disposing of acid

gas by injecting into a suitable reservoir – acid gas injection (Sharma & Campbell 1969).

In the transmission of natural gas further condensation of water is problematic. It can increase pressure drop in the line and often leads to corrosion problems. Thus, water should be removed from the natural gas before it is sold to the pipeline company.

For these reasons, the water content of natural gas and acid gas is an important engineering consideration (Sharma & Campbell 1969).

## Literature Review

Sour natural gas contains hydrogen sulfide ($H_2S$), which has to be removed to meet specifications for sales gas. Sour natural gas also contains carbon dioxide ($CO_2$). The removal of $CO_2$ and $H_2S$, usually called acid gases, from sour natural gas is generally accomplished by means of a regenerative solvent. There are several amine solvents used for this purpose. Upon regeneration of the solvent, the acid gases are liberated, and are usually sent to a modified Claus plant, where the $H_2S$ is converted to elemental sulfur (Canjar & Manning 1967). The acid gas stream to the modified Claus plant consists of $H_2S$, $CO_2$, water vapor and minor amounts of hydrocarbon gas.

When the concentration of $CO_2$ is considerably greater than the concentration of $H_2S$ in the acid gas mixture, the Claus plant has difficulty in achieving a high sulfur recovery. If the total sulfur rate is small, say less than 5 tons per day, it may be more economical to recover the sulfur by some other process. Such other processes, however, have many drawbacks of their own (Canjar & Manning 1967).

An alternative to recovering sulfur is to compress and reinject the acid gases into a suitable underground zone, in a manner similar to the disposal of produced water. An additional benefit of reinjecting the acid gases is the elimination of emission of sulfur compounds as well as $CO_2$ to the atmosphere (Canjar & Manning 1967).

### *Properties of $H_2S$ and $CO_2$*

Upon removal of the acid gases $H_2S$ and $CO_2$ from the sour gas, an acid gas mixture is obtained at low pressure that may also contain about 1 % to 3 % hydrocarbon gases, and which is saturated with water vapor (West 1948). This is the mixture that is compressed through 4 stages of compression, from about 100 kPa (ga) to around 8 to 10 MPa. In this process, water condenses, creating the potential for corrosion and hydrate formation. In addition,

at such final compressor discharge pressures, the acid gas becomes a liquid or a dense phase when cooled to ambient temperatures (West 1948).

While experimental results of studies of the physical properties of acid gas mixtures without hydrocarbon components are difficult to determine in the technical literature, the properties of pure $CO_2$ and $H_2S$ have been examined and reported (West 1948).

Additionally, the properties of each of the acid gases have also been studied in the presence of water at elevated pressures and temperatures.

These results can be used as a guide to indicate how the mixed acid gas streams would behave under the conditions of pressure and temperature when compressed to the injection pressure level.

A brief review of the properties of the pure acid gases and the $CO_2$ - water and $H_2S$ - water binaries is therefore appropriate.

### Vapor / Liquid Properties of Pure Compounds

In their pure state, $CO_2$ and $H_2S$ exhibit the normal vapor / liquid behavior with pressure and temperature. At higher pressure and temperatures, the pure compounds exist as liquid and vapor. Methane ($CH_4$) also exhibits this behavior, but at much lower temperatures. From this it can be seen that $CO_2$ and $H_2S$ can readily be liquefied at elevated pressures and at relatively high temperatures, whereas $CH_4$ can be liquefied only at very low temperatures (Song & Kobayashi 1989).

Mixtures of the acid gases are also readily liquefied at elevated pressures, but not mixtures containing substantial amounts of $CH_4$ in their makeup.

### $CO_2$-Water and $H_2S$-Water Mixtures

When a mixture of $CO_2$ or $H_2S$ and water is subjected to elevated pressures, another phase, namely a solid hydrate phase, is formed under certain conditions of temperature and elevated pressures. Hydrates can form at elevated pressures and at fairly high temperatures with $H_2S$, and at somewhat lower temperatures with $CO_2$ (Song & Kobayashi 1989). These pressures and temperatures are usually encountered in acid gas injection processes.

### Water of Saturation for $CO_2$ and $H_2S$

The ability of the pure compounds to hold water in the vapor phase is reduced as the pressure increases at about 2.7 MPa for $H_2S$ and up to about 6 MPa for $CO_2$. When pressures are raised above these levels, the capacity of $H_2S$ and $CO_2$ to hold water in solution increases substantially, as both compounds have a higher water absorption capacity in the liquid phase or dense phase as compared with their vapor phases (Song & Kobayashi 1989). A small amount of methane reduces substantially the water absorption ability of $CO_2$ at elevated pressure.

Other water content data at various temperatures and pressures for $CO_2$ and $H_2S$ are illustrated in Figures 20-4 to 20-7 of the *GPSA Engineering Data Book*, on page 20-5 of the 1994 edition.

### Acid Gas Mixtures

It is well known in the natural gas industry that raw sour natural gas mixtures present increased problems as compared to sweet natural gas in mainly two areas: increased potential for corrosion and increased propensity for the formation of hydrates at elevated pressures. It is therefore assumed that acid gases with little or no hydrocarbon content will further exacerbate these two problems. In actual fact, this may not be the case.

### Problem of Corrosion

Corrosion of low alloy steel by sour gas occurs mainly in the presence of a liquid aqueous phase. The corrosion manifests itself as general metal loss corrosion or pitting corrosion (Selleck et al. 1952). When these occur, atomic hydrogen is generated, which has the ability to penetrate steel. This can lead to hydrogen induced cracking, blistering or sulfide stress-cracking, resulting in sudden failures of the confining pipes or vessels. By following the *NACE MR0175* standard in materials selection and adhering to recommended construction practices, such failures can usually be avoided.

By dehydrating sour gas, corrosion by $H_2S$ or $CO_2$ is effectively eliminated. Similarly, the potential for corrosion by acid gas can also be controlled by dehydration.

### Problem of Hydrates

The hydrate forming temperature at any pressure of a sour natural gas increases with increasing content of $H_2S$. The opposite is the case with $CO_2$. For sour natural gases with low concentrations of $H_2S$, the concentration of $CO_2$ is usually much greater than the concentration of $H_2S$ (Wiebe & Gaddy 1941). Thus the acid gas mixture, upon

extraction from the sour gas, would be mainly $CO_2$. Hydrate temperatures at $H_2S$ contents below 5 % are no higher than what would be the case for sweet natural gas. Hydrates of course will not occur if the gas has no liquid water phase.

### Vapor / Liquid Phase Behavior

Any gas can be liquefied if it is sufficiently cooled. This means that aerial cooling readily liquefies acid gas mixtures at elevated pressures. If the acid gas mixture contains considerable amounts of light hydrocarbon gas, then the two-phase envelope for the mixture becomes wider in temperature – an example being a mixture that contains 10 % $CH_4$ and 45 % each of $H_2S$ and $CO_2$ (Song & Kobayashi 1984).

To completely liquefy such mixtures requires somewhat lower temperatures. If the acid gas mixture is ultimately to be liquefied upon compression and aerial cooling, then the sour gas treating plant must be designed and operated to minimize the hydrocarbon gas content of the acid gas mixture. The design should include a rich solution flash tank, and this vessel should be operated at a low pressure so that most of the dissolved hydrocarbon gas can be liberated. The solvent should be operated at the upper range of solvent concentration, and solution circulation should be such that the mole loadings (moles of acid gas picked up in the contactor per mole of solvent circulated) are also at the upper range of the recommended loadings (Song & Kobayashi 1989).

### Water Vapor Content

A high hydrocarbon content also adversely influences the water carrying capacity of the acid gas mixtures at high pressures. The equilibrium water vapor content of natural gas decreases with increasing pressure at constant temperature. Similarly, in their pure state, both $H_2S$ and $CO_2$ hold less water in the vapor phase as the pressure is increased. However, in the liquid or dense phases of $H_2S$ and $CO_2$, the water of saturation increases substantially with increasing pressure at a given temperature, due to the molecular attraction between these polar compounds (Song & Kobayashi 1984).

It is reasonable to assume that the behavior of mixtures of $H_2S$ and $CO_2$ would be similar to their behavior in the pure states. If this assumption is correct, then the acid gas mixtures without hydrocarbon content will also show a minimum water content at a pressure of about 3000 to 5000

kPa, depending on the relative amounts of $H_2S$ and $CO_2$ in the mixtures. Thus, by separating the condensed water in this pressure range and at a temperature a few degrees above the hydrate temperature, no free water should be present upon compressing the acid gases to substantially higher pressures and cooling to ambient temperatures (Song & Kobayashi 1984). At such elevated pressures, the acid gas mixture would be in the liquid phase or the dense phase at normal pipeline temperatures. This means that there may not be any need to dehydrate the acid gas mixture, as no liquid water phase would form after the final stage of compression and upon cooling to ambient temperatures. Without liquid water present, no hydrates would occur in the liquid phase of the acid gas mixture, and corrosion would be at a minimum (Selleck et al. 1952).

### Acid Gas Compression and Dehydration

The acid gas is liberated from the sweetening solvent in the regenerator tower, and this overhead vapor stream is then cooled. Most of the water and solvent is condensed in the cooler, and the two-phase mixture flows to the reflux drum, where the condensed liquids are separated and returned to the regenerator column as reflux. The vapor stream leaving the reflux drum contains the acid gases, $H_2S$ and $CO_2$, a small percentage of hydrocarbon gas and some water vapor (Wiebe & Gaddy 1941).

The pressure of this gaseous mixture is generally in the order of 80 to 100 kPa (ga), and at a temperature between 20°C in winter and up to 40°C in summer. This is the stream that would normally be sent to a flare stack if the sulfur content is less that 1 t/d, or be sent to a sulfur recovery unit if the sulfur content is 1 t/d or greater. If the acid gas contains more than say 60% $CO_2$, which is usually the case with small amounts of $H_2S$ in the sour natural gas, then a modified Claus plant may not be the best choice for small-scale sulfur recovery, and instead a redox unit could be selected to convert the $H_2S$ to sulfur (Song & Kobayashi 1989). However, redox processes are expensive to install, difficult to operate, and the resulting sulfur product does not meet the sulfur sales specifications.

### Compressor Discharge Pressure

The ultimate pressure to which the acid gas has to be compressed depends on the pressure of the reservoir, the permeability of the zone, and the depth of the zone. If the acid gas mixture is compressed to about 6000 kPa and

cooled below 20°C, the mixture will be in the liquid phase, provided the methane content is no greater than one or two percent (Wiebe & Gaddy 1941). The density of a liquid acid gas mixture at such conditions will have a density of about 70 to 80 % of the density of water. Thus the density of the acid gas stream in the liquid state will aid the injection pressure into the reservoir. Also, the rate of injection will be generally low, less than 1 Bbl/min. One Bbl/min. of liquid $CO_2$ injection amounts to about 100 10 $_3m_3$/d or 3.6 MMscf/d of gaseous $CO_2$ at standard pressure and temperature. Many zones have a pressure near the hydrostatic head of water (Selleck et al. 1952).

Thus the wellhead injection pressure would generally be in the order of 6000 to 9000 kPa, and would depend largely on the injectivity of the reservoir as well as reservoir pressure and depth. A four – stage compressor, can achieve the pressure of 6000 to 9000 kPa.

Table 1 shows the typical operating pressures for a four – stage compressor at a compression ratio of 3 between stages, and Figure 5 presents the variation in temperature between stages for an acid gas mixture containing 1% $CH_4$, 49% $C_2$ and 50% $H_2S$. The hydrate temperature with increasing pressure is shown with dashes.

*Table 1. Typical Interstage Pressures for a Four-Stage Compressor*

| Stage No. | Suction P., kPa (abs.) | Discharge P., kPa (abs.) |
|-----------|------------------------|--------------------------|
| 1 | 150 | 455 |
| 2 | 385 | 1160 |
| 3 | 1090 | 3270 |
| 4 | 3200 | 9600 |

(Song & Kobayashi 1984)

The total horsepower requirement in the above example is about 7.94 kW per 10 $_3m_3$/d (300 HP per Mmscf/d).

## *Cooler After Final Compression Stage*

If the acid gas is to be cooled after the final stage of compression so that it is converted into a liquid or dense phase, the final cooler section has to be designed to remove the equivalent of the latent heat of condensation of the acid gas. In Figure 5, for example, the heat removed during cooling after the fourth stage is about four times that removed after the third stage.

## *Metallurgy*

The compressor cylinders will compress gas that is at its water dew point on the suction side, and under-saturated in the compressor cylinder and on the discharge side, due to the temperature rise as a result of compression. Thus carbon steel meeting *NACE MR0175* standard requirements for sour gas should be installed as a minimum. The line to the aerial cooler can be carbon steel meeting the *NACE* standard. In the inter-stage coolers, water will condense, and could pose a corrosion problem. Downstream of the coolers, the lines to the inter-stage scrubbers and the scrubbers themselves will be exposed to the corrosive acid gas and condensed water mixture. Carbon steel meeting *NACE* specifications for sour gas, coupled with an appropriate corrosion inhibition program, should be all that is required to handle these corrosive fluids.

After the third stage of compression, the pressure will be in the order of about 3000 to 4000 kPa. This is the final stage at which water will condense in the cooler. Upon boosting the pressure substantially above 6000 kPa, the acid gas mixture can hold more water in solution than at the previous separation stage. Thus upon cooling after the fourth compression stage, there should theoretically be no water of condensation dropping out (Song & Kobayashi 1989). If this is so, then there would be no need to dehydrate the gas, and the downstream facilities could be constructed out of carbon steel meeting *NACE* specifications, which would save the gas industry a lot of money. This aspect of acid gas phase behavior should be experimentally investigated.

If dehydration is chosen to ensure that no water of condensation drops out at the high pressures, the dehydration should take place after the second or third stage of compression. When dehydration occurs after the second stage, the pressure is relatively low, but the acid gas mixture contains more water than after the third stage compression and cooling. With dehydration occurring after the third stage, the operating pressure of the dehydrator would be about 3 times the pressure after the second stage of compression. This would require less glycol circulation, smaller vessel diameter, but the amount of acid gases absorbed per gallon of glycol circulated would be higher. However, glycol circulation would need to be about one half of the required circulation for dehydration after the second stage of compression, since there is less water to remove from the acid gas stream at the higher pressure (Selleck et al. 1952).

In general, the selected metallurgy would depend on whether the gas is dehydrated or not. Stainless steel equipment includes the suction scrubbers, pulsation bottles, interconnecting piping and cooler tubes. The metallurgy of valves and instrumentation such as block valves, dump valves, PSV's, gauge glasses, etc., should generally match the material of the vessel and piping.

Compressor cylinder material can be carbon steel. Compressor suction and discharge valves should be stainless steel. The piston rod should be stainless steel, and may be coated with a tungsten carbide overlay having a maximum hardness of RC22. Distance pieces can be single compartment with a vacuum pump, or a two-piece compartment with a sweet gas purge system (Royan & Wichert 1995).

Because of the low suction pressure in the 1st stage suction scrubber, any liquids must be dumped to an atmospheric tank, or handled by a pump. Any liquids condensing in the remaining suction scrubbers are usually dumped to a sour water treatment and disposal system. Ideally, these liquids should be returned to the amine system, to save on make – up water. However, due to potential contamination with compressor oil, it is safest to discard the water that condenses in the suction scrubbers (Royan & Wichert 1995).

Compressor Units can be equipped with separate cylinder lubrication and flushing oil systems so that lube oils and corrosion inhibitors can be injected separately. Corrosion allowance in piping generally should be 3 mm in carbon steel materials and 1.5 mm in stainless steel materials (Royan & Wichert 1995).

### Acid Gas Dehydration

Whether or not acid gas dehydration is necessary is debatable. As mentioned above, under certain conditions of pressure and temperature, no water of condensation would occur after the final stage of compression (Canjar & Manning 1967).

If dehydration is installed, then it should be part of the process at pressures of minimum water content in the acid gas stream. At a temperature of about 35 °C after cooling, the optimum pressure range is 3000 to 5000 kPa, depending on the acid gas composition. This is the pressure range in which acid gas mixtures should exhibit a minimum equilibrium water content at the process operating temperature range (Song & Kobayashi 1984).

The dehydration equipment would be a normal glycol unit, with a minimum of six trays, using triethylene glycol.

In sales gas dehydration, the water content has to be reduced to about 65 mg/m3 (4 Ibs/MM). Since the objective in acid gas dehydration is simply the avoidance of a liquid water phase, the amount of water left in the acid gas can be substantially higher than 65 mg/m3. A safe water content would be about 500 to 700 mg/m3 (0.5 to 0.7 kg/103m3) (Song & Kobayashi 1984). Thus, the dehydration facilities for acid gas could be operated more economically than for sales gas dehydration.

One of the problems with dehydration of gas in general and with acid gas in particular is the disposal of the reboiler off-gases (Wiebe & Gaddy 1941). There is considerable environmental concern with venting these off - gases into the air. In acid gas dehydration, these off-gases have to be collected and incinerated or cooled and recompressed into the acid gas steam.

### Acid Gas Injection Facilities

The acid gas injection facilities beyond the final stage of compression and cooling consist of an injection line, well-site control facilities and the injection well.

### The Disposal Line

Selection of the type of pipeline material for the acid gas injection line between the plant and the injection well is generally related to whether or not the acid gas has been dehydrated. For dehydrated gas, sour service carbon steel materials can be used, such as CSA-Z662 Grade 359 Cat. II sour service material. The addition of corrosion inhibitor should be considered.

For non-dehydrated acid gas, the line can be of carbon steel with an internal epoxy coating, or a polyethylene liner (EPA 1995).

Another pipeline material can be 316L stainless steel. One of the key considerations is the length of the line. Stainless steel is more expensive, and if the cost of the line exceeds the cost of a dehydration unit, then it may be more economical-to dehydrate the acid gas stream. The proposed pipeline should be fully evaluated with the vendor of the materials to ensure compatibility with anticipated process conditions of pressure, temperature and acid gas composition (EPA 1995).

The line diameter should be sized for liquid phase fluids if the acid gas mixture contains no more than about 1 % hydrocarbons (EPA 1995). This means that the injection rates would be quite low in terms of liquid quantities.

The following formulae relate acid gas injection rates at standard conditions to liquid disposal volumes per minute:

$q_1$, liters/min = Q, acid gas $10_3 m_3$/d * (1.57* mol fr $CO_2$ + 1.27 * mol fr $H_2S$)

$q_1$, US gal/min = Q, acid gas MMscf/d * (11.8* mol fr $CO_2$ + 9.34 * mol fr $H_2S$)

(EPA 1995).

The superficial liquid velocity in the pipeline should be kept below 3 m/sec (10 ft/sec). Liquid velocity can be estimated by:

v, m/sec = 21.2 * liter/min / ($d_2$), where d is the internal diameter of the pipe, in mm

v, ft/sec = 0.409 * US gal/min / ($d_2$), where d is the internal diameter of the pipe, in inches

(EPA 1995).

From the above it can be seen that an injection rate of 28 $10_3 m_3$ /d (1 MMscf/d) of $CO_2$ reduces to 44 L/min (11.8 US gal/min) in the liquid phase. Thus the pressure drop in a short, 50 mm diameter line would be quite small, at a liquid velocity of about 0.37 m/sec. If the disposal well is near the plant site, a 50 mm disposal line out of 316L SS would cost about $ 40,000 (EPA 1995).

Under normal operating conditions the line between the plant and the injection well would contain the acid gas mixture in the liquid phase or the dense phase. The temperature of the fluid in the line would be at ground temperature, which could be as low as 0 °C in the winter. If this line had to be depressurized, however, very low temperatures would result in the line. Since the fluid would be blown down to atmospheric pressure, the temperature of the fluid in the line would decrease to the boiling point temperature of the acid gas mixture at atmospheric pressure (EPA 1995). This could be as low as - 50 °C, or lower if the line were insulated. Lines that are not insulated would benefit from heat transfer from the surrounding soil. The pipeline material has to be designed for low temperatures, even though under normal conditions such low temperature would not be reached. A safe blow-down design and procedure should be incorporated in such a scheme (EPA 1995).

The extremely low temperatures can be avoided by installing a 25 mm carbon steel line to the well site in the trench with the 50 mm injection line. The design

pressure of this sweet gas line would be 7 MPa, and under normal circumstances, this line would be left idle at a low pressure. The line would be connected at the well site to the injection line upstream of the wellhead (EPA 1995). If it became necessary to depressurize the injection line, the acid gas would be flowed back to the plant and into the flare system through a standby heat exchanger or a rental line heater. The liquid acid gas mixture would be heated and vaporized prior to the pressure reduction into the plant flare system. To prevent the acid gases from vaporizing in the injection line, sweet gas from the plant would be flowed to the well site through the 25 mm line, from where the sweet gas would push the acid gas fluids back to the plant at full pressure (EPA 1995).

## *Well site Facilities*

At the well site, the facilities would be very simple. A meter should be installed to record the flow. This would provide information to the plant SCADA system concerning the injection pressure, temperature, rate and the fluid density. The wellhead would be equipped with a check valve as well as an ESD valve (EPA 1995).

## *The Injection Well*

When an acid gas disposal scheme by downhole injection is considered, one of the first questions that arises is whether there is a suitable injection well within a reasonable distance, and the second question is whether the AEUB will permit injection of the acid gas into the particular zone that the well is completed in. In general, the Board will allow injection into the zone from which production is being taken provided the operator gives reasonable assurance that the injected acid gas will not adversely affect offsetting wells or hydrocarbon recovery (EPA 1995). A well some distance from the plant may not be the best choice, however. Firstly, it usually is not a part of the production scheme to the plant because it missed the producing horizon, or it is so tight that it is incapable of production. In such cases it may not be a suitable candidate for acid gas injection either.

The ideal acid gas injection well would be a well drilled for this purpose within 200 m of the plant perimeter. The zone chosen for acid gas injection should be a zone that contains salt water, which means that the zone in the plant area has no commercial value. Such zones tend to have good thickness, a high permeability and a good aerial extent (EPA 1995).

The drilling and completion costs are largely dependent on the depth of the horizon. Table 2 shows the cost estimates for drilling acid gas injection wells to 1500 and 2500 m in Alberta, and completing them with 73 mm J55 EUE tubing that is internally coated for corrosion protection.

*Table 2. Cost Estimate To Drill And Complete Acid Gas Disposal Well In Alberta*

| Depth, m | Drill & Case | Complete | Total Cost |
|---|---|---|---|
| 1,500 | $350,000 | $150,000 | $500,000 |
| 2,500 | $550,000 | $250,000 | $800,000 |

(EPA 1995).
The completion would include a downhole cheek valve, for safely reasons in case of surface equipment failure. A downhole packer would protect the casing and a non-corrosive fluid, such as diesel fuel containing corrosion inhibitor, in the annulus between the casing and tubing, as is normally required for water injection or disposal wells.

## Cost Comparisons with Small Scale Sulfur Recovery Options

In a companion paper, the various options for small-scale sulfur recovery are discussed (Royan & Wichert 1995). The capital cost of any of sulfur recovery process depends, of course, on many variables, such as the plant design throughput, composition, location, etc. The comparative costs can best be illustrated by an example:

> Estimate the capital cost of the sweetening facilities and the various sulfur recovery and disposal facilities for a sour gas plant designed to treat 500 10$^3$m$^3$/d of gas with 2.0 % $CO_2$ and 0.44 % $H_2S$.

(Royan & Wichert 1995)
The total sulfur content in the inlet gas stream in the above example is 2.98 t/d. The acid gas stream will contain 18 % $H_2S$, unless some $CO_2$ is left in the sweet gas by the chosen solvent. For the purpose of this example it is assumed that all of the $CO_2$ will be extracted. The capital cost estimate for the equipment, without installation in the field, is shown in Table 3.

*Table 3. Estimate of Capital Cost of Various Sulphur Recovery Processes (Thousands of Dollars)*

| Process Equipment | | Two-stage Claus | One-stage Selectox | LO-CAT II | SulFerox | Acid Gas Injection |
|---|---|---|---|---|---|---|
| Sweetening | | 650 | 650 | 650 | 650 | 650 |
| Sulfur recovery: | | | | | | |
| | Facilities | 1,000 | 1,000 | 2,400 | 1,800 | 0 |
| | Catalyst | 6 | 40 | 0 | 0 | 0 |
| | S Filter/Melt | 0 | 0 | 300 | 300 | 0 |
| | Solvent | 75 | 75 | 300 | 300 | 0 |
| | Incin. /Stack | 150 | 150 | 0 | 0 | 0 |
| Acid gas Injection: | | | | | | |
| | Acid gas compr. | 0 | 0 | 0 | 0 | 650 |
| | Acif gas line (316SS) | 0 | 0 | 0 | 0 | 40 |
| | Injection well | 0 | 0 | 0 | 0 | 700 |
| Royalties | | 0 | 100 | 150 | 200 | 0 |
| Estimated Total | | 1,881 | 2,015 | 3,800 | 2,850 | 2,040 |

*Note: Estimated capital costs are for skid mounted equipment f.o.b. Calgary shop.*

(Royan & Wichert 1995)
The capital cost changes somewhat with the total plant throughput and the $H_2S$ content. If in the above example the total sour gas inlet rate to the plant were 900 10$^3$m$^3$/d, having a $CO_2$ content of 4 % and a $H_2S$ content of 0.12%, the capital cost estimate would be as per Table 4. In this case the sulfur inlet rate to the plant is 1.46 t/d, with the $H_2S$

concentration in the acid gas stream being 2.91 % (Royan & Wichert 1995).

To employ the modified Claus process in the second example requires that a process be added between the sweetening step and the Claus plant to enrich the acid gas sufficiently in $H_2S$ so that a modified Claus unit will operate satisfactorily.

*Table 4. Estimate of Capital Cost Of Various Sulphur Recovery Processes (Thousands Of Dollars)*

| Process Equipment | | Two-stage Claus | One-stage Selectox | LO-CAT II | SulFerox | Acid Gas Injection |
|---|---|---|---|---|---|---|
| Sweetening | | 1,250 | 1,250 | 1,250 | 350 | 1,250 |
| Sulfur recovery: | | | | | (See note 2) | |
| | Acid gas enr. | 750 | 0 | 0 | 0 | 0 |
| | Facilities | 750 | 800 | 1,900 | 1,550 | 0 |
| | Catalyst | 5 | 20 | 0 | 0 | 0 |
| | S Filter/Melt | 0 | 0 | 300 | 300 | 0 |
| | Int. Chem. Chg. | 225 | 75 | 250 | 250 | 0 |
| | Incin. /Stack | 150 | 150 | 0 | 0 | 0 |
| Acid gas Injection: | | | | | | |
| | Acid gas compr. | 0 | 0 | 0 | 0 | 1,000 |
| | Acif gas line (316SS) | 0 | 0 | 0 | 0 | 40 |
| | Injection well | 0 | 0 | 0 | 0 | 700 |
| Royalties | | 200 | 100 | 150 | 200 | 0 |
| Estimated Total | | 3,300 | 2,395 | 3,850 | 2,650 | 2,990 |

*Note 1. Estimated capital costs are for skid mounted equipment f.o.b. Calgary shop*

*Note 2. 4% $CO_2$ left in sales gas*

(Royan & Wichert 1995)

Each of the sulfur recovery processes would release the CO2 to the atmosphere, amounting to 6,800 and 24,500 tons annually for the two cases, respectively.

## *Operating Costs*

Operating cost estimates for all processes are given in Table 5 and include of the following items:
- Utilities (electricity, fuel gas, water)
- Chemicals (catalyst, chelates, iron oxide ions, pH control, corrosion inhibitor)
- Maintenance
- Operator time

*Table 5. Estimate Of Annual Operating Cost Of Various Sulphur Recovery Processes (Thousands Of Dollars, For Example 1 Above)*

| Cost Item | Two-stageClaus | One-stage Selectox | LO-CAT II | SulFerox | Acid Gas Injection |
|---|---|---|---|---|---|
| Electr. Power | 76.3 | 95.5 | 78.4 | 104.0 | 153.3 |
| Fuel gas | 7.50 | 75.0 | 75.0 | 0 | 75.0 |
| Catalyst | 2.0 | 13.0 | 0 | 0 | 0 |
| Chemicals | 25.0 | 25.0 | 320.0 | 350.0 | 25.0 |
| Labor, Op/Mnt | 150.0 | 150.0 | 250.0 | 250.0 | 200.0 |
| Sulfur Disp. | 0 | 0 | 50.0 | 50.0 | 0 |
| Estimated Total | 328.3 | 358.5 | 773.4 | 754.0 | 453.3 |
| $ Per ton of S | 301 | 330 | 711 | 693 | 416 |

Assumptions going into these cost estimates:
- Catalyst change-out: once per 3 years
- Electricity: 10 c/kWh
- Fuel gas: $1.50/GJ
- Chemicals: routine consumption

(Royan & Wichert 1995)

The above cost estimates are for the first example, and include operator time. The costs for sulfur recovery schemes will not very that much between the two examples, as the overall amount of sulfur recovered is not that large to begin

with. Regarding acid gas compression, however, the costs would be higher in the second example by about $155 thousand in light of more compression for the higher acid gas rate.

### Optimum Acid Gas Injection Scheme

In light of the above discussions, it is possible to project what a minimum acid gas compression and injection scheme would include – as discussed below:

### Injection Well

The injection well should be drilled specifically for the purpose of acid gas injection. It should be located near the plant, so that the injection line would be short, and it would be within the Emergency Planning Zone of the plant. This would minimize the cost of the pipeline. The selected zone should be an aquifer of large extent, with good permeability. This means that the gas would not be reproduced, as would potentially be the case if the gas were injected into a hydrocarbon-bearing zone (EPA 1995).

The depth of the well should be between 1000 and 1500 m, so that the injection pressure did not have to be above 8000 kPa. This pressure level would ensure that the acid gas mixture is in the liquid phase upon final cooling, which would aid with the injection into the zone.

The well could be completed with 114.3 mm casing string and a 60.3 mm OD J-55 tubing string, as the liquid injection rate would in all likelihood be less than 100 L/min (27 US gal/min), thereby saving on drilling and completion costs. A subsurface check valve should be installed in the tubing (EPA 1995).

### The Injection Line

Since the well would be located near the plant, the injection line would be relatively short. A 316L stainless steel line, 50 mm in diameter, would likely be the best choice. This line would need to be externally coated for corrosion protection, but would not need to be insulated (EPA 1995).

Under normal operating conditions, the acid gas liquid or dense stream would not cool sufficiently to have water drop out to cause problems. If the line were shut down for some time, the contents of the line would cool down to ground temperature at burial depth, which would generally not be below 0 °C (EPA 1995).

Any water that might drop out would be minimal, would form a hydrate, and would immediately be reabsorbed upon startup of injection. A small, high pressure, sweet gas line should be included from the plant to the well, for reasons explained above.

### Water Removal

It is evident that free water cannot be tolerated at the injection pressure levels of the acid gas mixture, because hydrates could form. There is a minimum water of saturation content at certain pressure and temperature conditions. By taking advantage of this situation, it may be possible to lower the water content sufficiently by cooling the acid gas stream, so that dehydration would not be required (EPA 1995).

A more economical method than dehydration would be to cool the gas stream to about 30 or 35 °C after the third stage of compression. The cooling could be done with an aerial cooler to about 3 or 4 degrees above the hydrate temperature for the particular acid gas composition. This would condense most of the water while the acid gas mixture is in the vapor phase (EPA 1995). Upon compression and cooling after the fourth stage of compression, the acid gas stream would be in the liquid or dense phase. The water of saturation at the temperatures in the short line to the injection well would always be higher than the water content at the final separation stage. It is assumed in this example that the hydrocarbon content of the acid gas mixture is less than about 3 %. Higher concentrations of $C_{1+}$ will adversely affect this acid gas-water relationship (EPA 1995).

### Acid Gas Compression

An estimate has to be made of the final pressure to which the acid gas stream has to be compressed. This depends mainly on the formation pressure, which depends on the well depth in undisturbed reservoirs. Other factors influencing the injection pressure are the permeability of the zone, the thickness of the zone and the rate of injection. Assuming that the necessary pressure is between 6 MPa and 10 MPa, a four-stage compressor should be used (EPA 1995).

Concerning the metallurgy of the compressor, the suction scrubbers, the suction and discharge lines and the coolers, some items may need to be stainless steel, but with research in the area of water content, some of the lines could probably be constructed with carbon steel meeting *NACE* specifications for sour gas applications.

## Conclusions

- The compression and reinjection of acid gas into an underground reservoir is technically feasible and economically viable, when compared with alternate methods of sulfur disposal.

- Research should be carried out to determine the water of saturation of acid gas mixtures containing up to 1% to 3 % methane, in the pressure range of 3 MPa to 10 MPa, and at temperatures between 0 °C and 40 °C. The results would establish whether the acid gas would need to be dehydrated to avoid the formation of hydrates under operating conditions of acid gas injection systems.

- Reinjection acid gas into an underground formation releases the minimum of greenhouse gases into the atmosphere when compared with the options for small-scale sulfur recovery.

- Of the various options for handling small volumes of acid gas, compression and injection into an underground zone provides the greatest flexibility in operation with changing throughput rate or fluctuating acid gas composition.

## *The Sharma – Campbell Method for Predicting Water Content*

Sharma and Campbell propose a method for calculating the water content of natural gas, including sour gas. Although originally designed for hand calculations, this method is rather complicated. It is even rather complicated for computer applications.

The method will be described here. Given the temperature and the pressure, the procedure is as follows. Determine the fugacity if water at the saturation conditions (T and $P_{sat\ water}$), which is designated $f_{sat\ water}$, and the fugacity at the water conditions (T and $P_{total}$), designated $f_{water}$. A chart is provided to estimate the fugacity of water at the system conditions. Then the correlation factor, k, is calculated from the following equation:

$$k = P_{sat\ water} \quad f_{sat\ water} \quad P_{sat\ water} \quad P_{total}^{0.0049}$$

$$P_{total} \quad f_{water} \quad P_{total} \quad P_{sat\ water}$$

(Sharma & Campbell 1969)

In this equation a consistent set of units should be used for the pressure and fugacity terms and then k is dimensionless. Then you must obtain the compressibility factor (z-factor), z, for the gas again at system conditions.

Sharma and Campbell recommend using a generalized correlation for the compressibility. Finally, the water content is calculated as:

$$w = 47484\,k \quad \frac{f_{sat\ water}}{f_{gas}}^{5}$$

(Sharma & Campbell 1969)

where f is the fugacity of the dry gas calculated at system conditions. Again, if a consistent set of units is used for the fugacity terms, then the calculated water content, w, is in lb/MMCF.
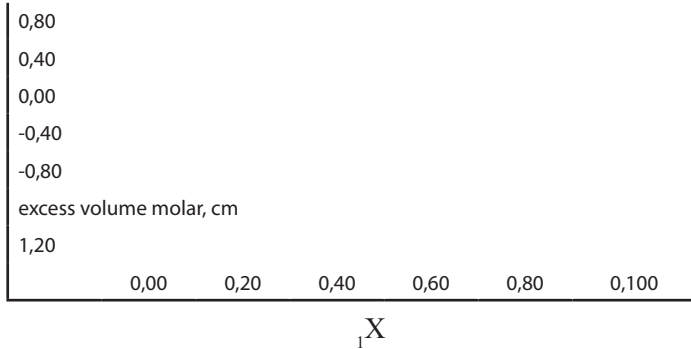
This method is rather difficult for hand calculations. First, it requires the compressibility factor of the gas mixture. Next, it requires the fugacity of pure water at system conditions. The chart given to estimate this value is only valid for temperatures between 80 and 160 degrees F, and for pressure less than 2000 psia (Sharma & Campbell 1969). It is unclear how this method will behave if extrapolated beyond this range. Typically, the calculation of a single fugacity is enough to scare away most process engineers. The Sharma – Campbell method requires three fugacity calculations for a single water content estimate.

The temperature and pressure limitations make this method less useful for some studies, where the pressure of interest usually ranges up to 10,000 psia and temperatures to 220 degrees F (Sharma & Campbell 1969). In addition, although this is intended to be a hand calculation method, it is a bit difficult to use.

## *The Eykman Molecular Refraction (EMR) Mixture Combination Rules*

For an example of the prediction of refractive indices, Eykman's mixing rules are displayed below:

| | A0 | A1 | A2 | A3 | A4 | s |
|---|---|---|---|---|---|---|
| 2-butanone (1)+1-chloropentane (2) | | | | | | |
| $V_E$, cm$_3$.mol$_{-1}$ | 2,64654 | 0,13115 | -0,00177 | 0,06722 | 0,00270 | |
| $R_E$, cm$_3$.mol$_{-1}$ | 0,36011 | -0,03642 | -0,00717 | 0,00785 | 0,00100 | |
| 2-butanone (1)+1,3-dichloropropane (2) | | | | | | |
| $V_E$, cm$_3$.mol$_{-1}$ | -0,49936 | 0,98856 | 1,31123 | 0,25639 | 0,00234 | |
| $R_E$, cm$_3$.mol$_{-1}$ | 0,16256 | 0,19454 | 0,11474 | 0,09188 -0,15178 | 0,00069 | |
| 2-butanone (1)+1,4-dichlorobutane (2) | | | | | | |
| $V_E$, cm$_3$.mol$_{-1}$ | -1,11593 | 0,72989 | 0,05418 | | 0,00280 | |
| $R_E$, cm$_3$.mol$_{-1}$ | 0,28129 | 0,42182 | -0,46736 | 0,02022 -0,10627 | 0,00074 | |
| 2-butanone (1)+1,1,1-trichloroethane (2) | | | | | | |
| $V_E$, cm$_3$.mol$_{-1}$ | 0,35307 | 0,62942 | 0,15189 | 0,04568 | 0,00009 | |
| $R_E$, cm$_3$.mol$_{-1}$ | 0,12084 | 0,14019 | 0,02597 | | 0,00013 | |
| 2-butanone (1)+1,1,2,2-tetrachloroethane (2) | | | | | | |
| $V_E$, cm$_3$.mol$_{-1}$ | -4,40442 | -0,26605 | -0,26976 | -0,09947 | 0,00032 | |
| $R_E$, cm$_3$.mol$_{-1}$ | -0,13382 | 0,34352 | -0,05271 | | 0,00017 | |

(Tasic et al. 1992)

```
0,80
0,40
0,00
-0,40
-0,80
excess volume molar, cm

1,20
         0,00   0,20   0,40   0,60   0,80   0,100
                        1X
```

- 2-butanone (1)+1-chloropentane (2)
- 2-butanone (1)+1,4-dicholorobutane (2)
- 2-butanone (1)+1,3-dichloropropane (2)
- 2-butanone (1)+1,1,1-trichloroethane (2)
- 2-butanone (1)+1,1,2,2-tetrachloroethane (2)

```
0,12
0,08
0,04
.mol
RE,cm3
-0,04
-0,08
         0,00   0,20   0,40   0,60   0,80   1,00
                        1X
```
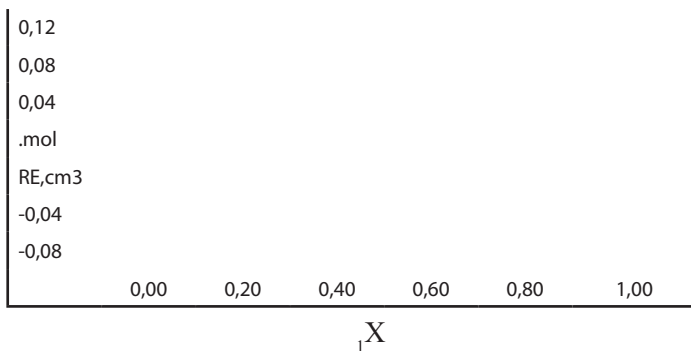
- 2-butanone (1)+1-chloropentane (2)
- 2-butanone (1)+1,4-dichlorobutane (2)
- 2-butanone (1)+1,3-dichloropropane (2)
- 2-butanone (1)+1,1,1-trichloroethane (2)
- 2-butanone (1)+1,1,2,2-tetrachloroethane (2)

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